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COMPLETE SPECIFICATION

Particulate Reflective Elements and method for forming the same

We, THE MEARL CORPORATION, a corporation organised under the laws of the State of New Jersey, United States of America, of 217 North Highland Avenue, Ossining, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention pertains to particulate reflective elements. More particularly, the invention relates to nacreous pigments having as nacre- and, if desired, color-producing components high refractive index metal sulfide layers.

In the following specification all parts and percentages are given by weight, unless otherwise indicated.

"Particulate reflective elements" are particles having relatively small dimensions of up to 10 millimeters, such as mica flakes, glass platelets, glass spheres, plastics particles, and lacquer- or resin-coated particles.

"Nacreous pigments" are substances which produce a pearly luster. The pigment particles are platelets, at least parts of which consist of substances of high refractive index. Such pearlescent pigments may be applied as surface coatings, as in simulated pearls, or may be incorporated in plastics, as in plastic pearl buttons. In general, a pearly or mother of pearl-like appearance can be obtained whenever the platelets are incorporated in a sufficiently transparent film or other body.

The earliest nacreous pigment, natural Pearl Essence, contained plate-like crystals of guanine obtained from fish scales and other fish tissues. Early synthetic nacreous pigments were composed of basic lead carbonate, lead hydrogen phosphate, lead hydrogen arsenate,

or bismuth oxychloride, all of which have relatively high refractive indices and are crystallizable in the form of platelets. Recently, more complex types of nacreous pigments have been developed. One such pigment is disclosed in Specification No. 992805. This pigment consists of platelets in which a layer of low refractive index, such as magnesium fluoride, is sandwiched between two layers of high refractive index, such as zinc sulfide. Another recently described complex nacreous pigment consists of coatings of titanium or zirconium oxide deposited upon transparent, lower refractive index particles.

If, as pointed out more fully hereinafter, the platelets of either the simple or complex types of nacreous pigment are provided in a particular range of thicknesses, and if the platelet thickness is sufficiently uniform, the nacreous pigment imparts color by light interference phenomena, as well as pearly luster to the object in or on which it is used. The color characteristics are unusual in that one color is seen by reflected and the complementary color by transmitted light. Such interference colored nacreous pigments are therefore capable of producing a color play which is not obtained with conventional colored pigments, where the color is produced by the absorption of certain wavelengths of light.

The sandwich type of nacreous pigment described in the application referred to hereinabove is produced by a vacuum evaporation procedure requiring the installation of relatively elaborate and costly process equipment. The preparation of the supported titanium or zirconium oxide pigments involves the use of less elaborate equipment, the pigments being formed by deposition from solution. Such procedure is disadvantageous, however, in that the titanium dioxide coating, for example, must

be calcined at an elevated temperature in order to produce a chemically stable film. Crystallization of the TiO_2 coating during the calcining operation leads to the formation of very tiny, microscopic crystallites which impair the smoothness and regularity of the coating. Thus, the pearl lustre and the color intensity (in those cases in which the coating is of interference film thickness) are decreased considerably from that which would be obtained with an ideal, smooth coating. The thicker the coating, the greater the loss of quality which may thus result.

We have found that nacreous pigments or other reflective elements may be provided by depositing zinc or other metal sulfides on particulate substrates at atmospheric pressure, without necessitating the use of the special equipment required for the vacuum evaporation procedure. Furthermore, the sulfide coatings thus obtained possess remarkably uniform thicknesses and are free of imperfections, even after heating operations. Also, such zinc sulfide coatings produce a degree of pearl brilliance and, when deposited in interference film thicknesses, color intensities not attainable with previously known coated titanium or zirconium oxide pigments.

There has been a need to provide such a nacreous pigment, and other particulate reflective elements, having high refractive index light stable sulfide coatings formed on particulate substrates, which coatings impart superior brilliance and, in the case of interference-colored elements, provide color intensities heretofore unavailable. There has also been a need to provide such reflective elements which may, if desired, be made luminescent. Also, there has been a need to provide a process for the preparation of such elements, which is both relatively simple and economical to perform and which facilitates the production of products having improved light stability and exhibiting superior uniformity of light transmission and reflection characteristics.

According to the present invention, there is provided a particulate reflective element comprising individual particles having maximum dimensions up to 10 millimeters and having high reflectivity and a nacreous lustre, wherein each particle includes a substrate which is constituted of mica, glass, plastic, or a lacquer or resin-coated substance, said substrate having deposited thereon at least one layer of a water-insoluble metal sulfide, said layer having an optical thickness Nd from 40 to 1,000 millimicrons, wherein " N " is the index of refraction of said layer and " d " is the thickness thereof, and said particles having maximum dimensions up to 10 mm.

There is also provided a process for preparing a particulate reflective element comprising individual particles having maximum dimensions up to 10 millimeters, which comprises:

- a) suspending smooth, plate-like supporting substrates for said particles in an aqueous solution containing (1) a water-soluble salt of a metal having a water-insoluble sulfide and (2) an organic sulfur-containing compound which releases sulfide ions in aqueous media, in an aqueous dispersion, said substrates being constituted of mica, glass, plastic or a lacquer or resin-coated substance;
- b) heating the resulting reaction mixture at temperatures of from 60°C . to the boiling point of the mixture for a period of from $1/4$ to 5 hours, with agitation, to produce a sulfide coating on said substrate particles while maintaining the same in suspension;
- c) separating the reflective particles thereby produced from said suspension;
- d) drying said particles to produce a light stable, reflective material.

Preferably, the dry particulate reflective materials are heated at temperatures of from 200° to $1,000^\circ\text{C}$. for periods of from 1 to 4 hours to increase their light stability.

A preferred embodiment of the invention also provides a nacreous pigment constituted of particulate platelets having maximum dimensions of from 3 to 100 microns and substantially smooth surfaces, each of said platelets including a mica substrate and a pair of high refractive index layers formed on the opposite faces of said substrate constituted of a water-insoluble metal sulfide, said layers having substantially uniform optical thicknesses Nd of from 40 to 1,000 millimicrons, wherein " N " is the index of refraction of the layer and " d " is the thickness thereof.

In the following detailed description, the invention is principally explained with reference to the production of nacreous pigments. It will, however, be understood that the preparation of other particulate reflective elements bearing the high refractive index stable sulfide coatings hereof and having maximum dimensions of up to 10 millimeters is within the scope of the present invention.

The nacreous pigment produced in accordance with the invention possesses a substantially uniform, imperfection-free sulfide coating which produces outstanding pearl brilliance and when deposited in interference film thicknesses, provides color intensities unmatched by previously known complex nacreous pigments. Moreover, by heating the precipitated sulfide coating, as indicated hereinabove, the nacreous layer is converted to a form providing markedly superior light stability characteristics, as compared, for example, with the complex titanium or zirconium oxide pigments discussed above.

Additionally, it has been found that the sulfide coated nacreous pigments hereof may be provided in interference film thicknesses

displaying higher order interference colors (which have the unusual optical effects described hereinafter) by a single deposition of the sulfide coating. When, on the other hand,

5 it is desired to produce such higher order interference films employing complex titanium dioxide nacreous pigments, it is necessary to utilize a multiple coating technique.

10 It is preferred to employ a zinc sulfide coated nacreous pigment in the practice of the present invention. Zinc sulfide is substantially colorless and does not, therefore, impart any inherent absorption color to the product pigment. Also, the color of such pigment is,

15 in the case of interference thickness sulfide coatings, entirely attributable to interference effects unless, of course, the pigment substrate has an inherent absorption color. Moreover, the zinc sulfide containing pigment provides

20 excellent light stability and may, if desired, be so prepared as to provide a luminescent nacreous pigment.

It is, however, possible to form nacreous pigments in accordance with the invention

25 incorporating other metallic water-insoluble sulfides, by reacting water-soluble salts or complexes of such metals with organic sulfur containing compounds. The sulfides of cobalt, lead, mercury, manganese, cadmium, arsenic,

30 antimony, nickel, iron, copper, bismuth or tin may, for example, be so employed. When, as indicated above the sulfide coating comprises zinc sulfide, the colors displayed by the coating are entirely attributable to interference

35 effects. With other sulfides, the colors are a combination of interference colors and the inherent absorption color of the particular sulfide. An SnS_2 coating, for example, of such thickness as to have a red interference

40 reflection color appears red when seen at some angles and yellow when seen at other angles. An NiS coating of a thickness which produces green reflection appears green at some angles and black at other angles. Accordingly, while

45 the following description is principally directed to the formation of a zinc sulfide coated nacreous pigment, in accordance with a preferred form of the invention, it will be understood that the invention includes within its

50 scope the production of nacreous pigments or other particulate reflective elements incorporating other high refractive index, water-insoluble metal sulfide coatings as specified hereinabove.

55 The thin sulfide coated pigment particles possess the characteristics of nacreous pigments displaying, in the case of zinc sulfide, a bluish or whitish reflection when the zinc sulfide layer has a thickness of from 20 to

60 m/μ . When the thin film or layer of zinc sulfide is slightly thicker the rays reflected from its opposite surfaces may interact, resulting in the reinforcement or destruction of light of certain wavelengths, the pigment particles thus appearing colored when they are

65 illuminated with white light.

Destructive interference of a given wavelength occurs if the reflections from the two surfaces of the film are completely out of phase. This occurs, for light perpendicularly

70 incident on the film, for wavelengths λ when

$$Nd = (n - 1) \lambda / 2 \quad (1)$$

where

"N" is the index of refraction of the film

75 "d" is its thickness, and

"n" is a small integer, e.g., 1, 2, 3, etc.

If the incident light is monochromatic and of wavelength λ , this well-known equation predicts that there would be no reflection at all. If, on the other hand, the film is illumin-

80 ated by white light, all wavelengths except λ appear in the reflection.

Reinforcement of a given wavelength occurs if the reflections from the two surfaces of the film are in phase with one another. For light

85 perpendicularly incident on the film, this occurs when

$$Nd = (2n - 1) \lambda / 4 \quad (2)$$

the terms being defined as above.

The index of refraction N for zinc sulfide

90 is about 2.3. The smallest film thickness which can produce color by destructive interference is that which will cause the shortest wavelength in the visible spectrum, i.e., violet blue, to be eliminated from the reflected light.

95 Taking λ for light of this color as $400 \text{ m}\mu$ the thickness of the film necessary to produce this effect is approximately $87 \text{ m}\mu$.

The resulting reflected light has the color complementary to that which is eliminated

100 from the reflection, or yellow in the present instance. Thus, the thinnest film capable of producing a color by destructive interference has a yellow reflection color. Films which

105 reflect red, violet, blue, and green are progressively thicker.

Beginning at violet, the reflection color which is produced by the elimination of a particular wavelength is enhanced by a reinforcement

110 color in accordance with Equation (2).

The approximate thicknesses of the zinc sulfide films necessary to produce nacreous pigments displaying various interference colors are indicated in the following table:

TABLE I

Optical Thicknesses of Zinc Sulfide-Containing Nacreous Pigments

Reflection Color	Source	Approx. Optical Thickness, Nd (m μ)	Approx. Thickness (m μ) if N = 2.3
Yellow	Elimination of violet-blue- approx. 400 m μ	200	87
Magenta	Elimination of green, approx. 520 m μ	260	113
Purple	Elimination of yellow, 590 m μ Reinforcement of violet, 400 m μ	300	130
Blue	Elimination of orange, 610 m μ Reinforcement of blue, 480 m μ	320	139
Green	Elimination of red, 650 m μ Reinforcement of green, 520 m μ	360	156
2nd Yellow	Elimination of blue, 440 m μ Reinforcement of yellow, 590 m μ	440	191
2nd Red	Elimination of blue-green, 490 m μ Reinforcement of red, 650 m μ	490	213
2nd Blue	Elimination of yellow, 575 m μ Reinforcement of blue, 460 m μ	575	250
2nd Green	Elimination of red, 650 m μ Reinforcement of green, 520 m μ	650	282

5 The description second (2nd) yellow, second (2nd) red, etc., is used herein to describe the second occurrence with increasing thickness of each of the colors, in preference to the terms "second order yellow", etc. The usual definition of higher order interference colors by order number is not always consistent with the value of "n" in interference equations (1) and (2) above, "n" also occasionally being referred to as order. Hence, the nomenclature given above has been here used instead.

10 Further increases in the thickness of the zinc sulfide layer, beyond that specified for

the second green reflection, result in the production of third reflection colors. The interference film displaying a third green has an approximate optical thickness of 1,000 m μ . Interference films having greater optical thicknesses do not possess the color intensity of the second and third colors and are relatively uneconomical to produce.

25 The interference colors thus provided are dependent upon the angle of observation (the colors indicated in Table I being those displayed at perpendicular incidence), the colors shifting to the wavelengths which correspond

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to thinner films as the angle of incidence increases, i.e., as the direction of the incident light departs from the normal to the surface. The first reflection colors show a moderate shift of wavelength with variation of the angle of observation; hence, green goes to blue, blue to purple, magenta to orange, and gold to a pale yellow shade. The second colors, on the other hand, display a much wider shift of the reflected wavelength, second green changing to blue and then to purple with increasing angle of incidence, second blue changing to purple and then to red, second red changing to greenish-gold, and second gold changing to bluish-green. By coating such nacreous pigments displaying higher interference colors on dark, curved surfaces it will be seen that remarkable iridescent effects can be achieved. Similar effects may also be attained by incorporating the second interference film pigments in plastics, with the pigment particles oriented in non-planar patterns.

The nacreous pigments hereof are prepared by depositing the zinc or other sulfide from an aqueous solution, using an organic sulfur-containing compound as the source of sulfide. It has been found that the conventional method of forming zinc sulfide by bubbling H_2S gas through a solution of a zinc salt is highly unsatisfactory as a procedure for coating the particulate substrates employed herein. The precipitation of zinc sulfide with H_2S results merely in the formation of distinct ZnS particles, which show little or no tendency to coat and adhere to particulate material which may be present. It has been found, however, that a smooth, adherent film of ZnS may be deposited if the source of sulfide ions is an organic sulfur-containing compound such as thioacetamide, thiourea, thioglycolic acid, thioacetic acid, thioformamide, or thiosalicylic acid.

The source of zinc for the reaction is a zinc compound soluble in the aqueous medium, employed in an amount expressed as ZnO of from 0.25 to 7.5%, preferably from 0.5 to 3.5% of the solution. Suitable soluble salts include zinc acetate, zinc chloride, zinc sulfate, zinc formate and zinc nitrate. Zinc oxide may also be used, and is more economical for coating reactions carried out in strongly alkaline media.

The concentration of sulfur compound generally depends on the zinc concentration. An equimolar ratio of sulfur to zinc is desirable, but satisfactory results are obtained employing molar proportions from 0.5 to 3 moles sulfur per mole zinc.

The particulate substrate upon which the zinc or other sulfide coating is deposited, in accordance with the invention, is preferably in the form of substantially smooth platelets having a major dimension of from 3 to 100 microns, and preferably a thickness of from 50 to 2,000 millimicrons. Preferably, the sub-

strate material comprises mica platelets which are desirably those of muscovite. Other types of mica platelets may however also be used, such as biotite, plogopite, vermiculite, and various synthetic micas, especially those which resemble natural white mica. The mica particles preferably are of the "water ground" variety, of from 150 to 400 mcsh, and having surface areas, as determined by the BET method, of from 2 to 6 square meters per gram. Particularly satisfactory results have been obtained employing fractions which pass through 200, 325 or 400 mesh screens, and which are substantially free of very fine particles, the mesh being in terms of number of openings per linear inch.

While it is preferred to utilize mica platelets for the pigment substrate, other particulate materials having the dimensions specified hereinabove may be employed in accordance with the present invention. Hence, the nacreous pigment may also be formed by depositing the sulfide coating upon platelets constituted of glass or plastics.

The acidity or alkalinity of the reaction mixture is selected in accordance with the specific organic material utilized as the sulfide source. For example, when thioacetamide is so employed, the reaction is carried out in acidic solution, preferably within a range of from about pH 2.0 to 5.0, desirably from 3.5 to 4.5. The solution may be adjusted to the desired pH range, with, for example, formic acid, hydrochloric acid, sulfuric acid, or nitric acid.

The deposition reaction is carried out by heating the aqueous mixture containing the zinc salt, the organic sulfur-containing compound and the particulate substrate at elevated temperatures of from 60° C. to the boiling point of the aqueous system, for a period of from 1/4 to 5 hours. It will be understood that within the indicated ranges, longer reaction times are required when the reaction mixture is heated at lower temperatures. The mica or other substrate is maintained in suspension and the zinc sulfide coating deposited thereon in substantially amorphous form to produce the desired nacreous pigment.

The pigment particles are thereafter separated and dried, e.g., at 110° C. and, preferably, heated at temperatures of from 200° C. to 1,000° C. The light stability of the sulfide-coated pigment which has been dried at 110° C. and not subjected to a subsequent heating is markedly superior to the stability of unheated titanium dioxide complex nacreous pigments referred to hereinabove, the latter being subjected to severe chalking.

Desirably, however, the sulfide-coating pigment is subjected, after drying, to the heating at temperatures of from 200° to 1,000° C. in air or within an inert atmosphere. At the higher temperatures within the indicated range it is preferred to effect the heat treatment in

nitrogen or other non-oxidizing gas, e.g., helium, argon or carbon dioxide.

It has been found that the heating increases the density of the sulfide coating, causing an increase in the refractive index thereof which increases reflectivity and reduces the thickness of the film, shifting the interference colors accordingly. Zinc sulfide coated platelets subjected to such treatment retain their smooth surfaces whereas titanium dioxide coated pigments, for example, become somewhat roughened during the shrinkage accompanying the heat treatment. Such roughening tends to reduce specular reflectance and increase light scattering. The avoidance of light scattering from the coated platelets is of particular importance with coatings of interference thickness since smooth surfaces (which do not cause such scattering) provide maximum color intensity. Heating the sulfide coated pigment at temperatures of 200° C. or higher thus markedly increases light stability without impairing the smoothness of the coating surfaces.

Employing heat treatment temperatures of about 700° C. or higher, it has been found that substantially total conversion of the amorphous zinc sulfide coating to its crystalline form (sphalerite) is effected. This increase in crystallinity further increases light stability and has been found to produce a marked increase in refractive index and reflectivity of the pigment surfaces, unexpectedly without impairing the smoothness thereof.

The following examples illustrate preferred embodiments of the method for forming the particulate reflective elements of the present invention:

EXAMPLE 1

White Pearl Pigment

Zinc acetate dihydrate (40 parts by weight) and thioacetamide (14 parts) were dissolved in 890 parts of water. To the solution were added 48 parts of mica flakes (water ground muscovite with a surface area, as determined by the BET method, of 4 square meters per gram).

The suspension was brought to pH 4.0 with 43 parts of formic acid. The reaction mixture was thereafter heated to boiling with agitation to keep the mica well suspended, and refluxed for 90 minutes, after which the zinc sulfide-coated mica was filtered, washed with water, and dried at 110° C. to produce a lustrous white pearl product.

Microscopic examination by reflected light at 1,000 X magnification revealed a smooth and uniform zinc sulfide coating on the mica flakes.

Light stability of the resulting pigment was determined by coating pigment samples in a nitrocellulose lacquer employing a doctor blade device, and then subjecting the coatings to exposure. The coating formulation consisted of 4% of the coated flakes in a clear, unstabilized cellulose lacquer of the following composition:

Nitrocellulose 15/20 second RS type	3.0%
Nitrocellulose 30/40 second RS type	6.5%
Ethanol	5.1%
n-Butyl acetate	85.4%
	100.0%

After exposure for 55 hours, the nitrocellulose film had become slightly brown.

EXAMPLE 2

Light Stabilized Pearl Pigment

The dried flakes produced as described in Example 1 were heated for one hour at 300° C. in air. The light stability of the heated pigment was measured by making a 4% suspension of the coated mica flakes in nitrocellulose lacquer, and making the suspension into a sample which was tested for light stability as indicated in Example 1. Light stability was increased to 85 hours, as compared with the 55 hour period evidenced by the pigment produced in accordance with Example 1.

EXAMPLE 3

Light Stabilized Pearl Pigment

A further sample of the dried pigment produced in Example 1 was heated for one hour at 700° C. in nitrogen, and tested for light stability by the technique described above. The light stability was thereby increased to more than 100 hours.

EXAMPLES 4—11

Interference Colored Pigments

The procedure of Example 1 was repeated, except that the ratio of mica to zinc salt was decreased in order to obtain thicker zinc sulfide coatings which produced color by light interference phenomena. Several pigment samples were produced by reacting the zinc acetate dihydrate and thioacetamide in 890 parts water, employing sufficient formic acid in each case to adjust the acidity to pH 4.

The reactant proportions utilized (in parts by weight) to produce pigments displaying different interference colors are indicated in the following table:

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TABLE II
Interference Colored Zinc Sulfide-Mica Pigments

A. Reactant Proportions Employed

Example	Mica	$\text{ZnC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$	Thioacetamide	Formic Acid
4	35.5	48.0	16.5	51.6
5	33.2	49.7	17.1	53.5
6	26.2	55.9	19.2	60.0
7	22.5	57.7	19.8	62.0
8	21.2	58.7	20.2	62.2
9	20.0	60.0	20.6	64.5
10	16.0	61.8	21.2	66.5
11	14.0	63.7	21.8	68.5

B. Characteristics of Product Pigments

Example	Reflection Color	Approx. Nd	Thickness for N = 2.1
4	gold	200 mμ	Approx. 95 mμ
5	magenta	260 mμ	Approx. 124 mμ
6	blue	320 mμ	Approx. 152 mμ
7	green	360 mμ	Approx. 171 mμ
8	2nd gold	440 mμ	Approx. 210 mμ
9	2nd red	490 mμ	Approx. 233 mμ
10	2nd blue	575 mμ	Approx. 274 mμ
11	2nd green	650 mμ	Approx. 310 mμ

The indicated colors were those displayed by the coated flakes when seen against a black background.

- 5 The pigment products were heated at 500° C. for 60 minutes, the heating imparting markedly improved light stability to the pigments and effecting no significant changes in their colors. Examination of each of the product pigments by reflection microscopy at 1,000 X revealed that all the coatings thus formed were smooth and uniform and remained so even after heat treatment to improve light stability.

Further heating at 700° C. in nitrogen 15 caused a shift in color to that corresponding to a slightly thinner film, the coatings remaining smooth and uniform when examined by reflection microscopy at 1,000 X.

EXAMPLE 12 20
Plural Interference Colored Pigments Produced During a Single Deposition Operation
Since the nacreous zinc sulfide coating on the substrate particles builds up in a regular fashion, pigments of various colors may be 25
produced during the course of a single sulfide

deposition by periodically withdrawing pigment samples before the run is completed. For this purpose, the reactants of Example 11 were utilized in the precipitation procedure of Example 1, aliquot product portions being withdrawn after various time intervals. The flakes were dried at 110° C. and made into nitrocellulose samples. The reflection colors of the samples are indicated in the following table:

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TABLE III

Pigment Samples Produced During Single ZnS Deposition

Time after reaching Boiling Point	Reflection Color
35 min.	"white"
42 min.	gold
45 min.	red
47 min.	violet
50 min.	blue
54 min.	green
56 min.	2nd gold
60 min.	2nd red
65 min.	2nd blue
76 min.	2nd green

EXAMPLE 13

Luminescent Nacreous Pigment

500 parts of the dried product prepared in accordance with the procedure of Example 1 were mixed with 2 parts NaCl and 0.0211 part CuCl₂. The mixture was heated to 850° C. in about one hour, and then permitted to cool in the air. Finally, the product was washed with water saturated with H₂S.

The resultant phosphor luminesced green, with a moderate green afterglow, on radiation with ultraviolet light of wavelength 3650 Å. The inherent high reflectivity of the product increased the intensity of the fluorescence beyond that which is observed with ordinary luminescent zinc sulfide.

When other activators are substituted for the copper salt indicated above other luminescent characteristics may be obtained. Hence, the use of a manganese salt activator results in the production of an orange luminescent product, and a silver salt activator, for example, imparts blue luminescence to the pigment.

EXAMPLE 14

White Pearl Pigment on Glass Flakes

The Example 1 procedure was repeated, except that the quantity of water was doubled and the 48 parts of mica were replaced by 290 parts of glass flakes with an average

thickness of 1 to 2 microns. The coating reflected white light.

The product was first dried at 110° C., and then heat treated as in Example 2.

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EXAMPLE 15

White Reflective Elements on Glass

Spheres

The procedure of Example 1 was followed, except that the quantity of water was trebled and the mica flakes replaced by 580 parts of glass spheres with an average diameter of 30 microns and an index of refraction of approximately 1.5.

On incorporation in a clear paint vehicle, the glass spheres displayed greatly increased reflectivity as compared with the uncoated glass spheres.

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EXAMPLE 16

White Reflective Elements on Polystyrene

Beads

Example 1 was repeated, except that the quantity of water was doubled and the mica replaced by 390 parts of polystyrene beads averaging 1 mm in diameter. The surface of the polystyrene beads was slightly roughened by a 2-minute immersion in a solution consisting of 6% K₂Cr₂O₇, 74% H₂SO₄, and 20% H₂O. The coated spheres reflected white light.

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EXAMPLE 17

Pigment of SnS_2 Coated on Mica Flakes
Stannic chloride pentahydrate (31.9 parts) and thioacetamide (14 parts) were dissolved
5 in 800 parts of water. To the solution were added 48 parts of mica flakes. The suspension had a pH value of approximately 0.5.

The reaction mixture was heated to boiling with agitation, and refluxed for two hours.
10 The stannic sulfide-coated mica was filtered, washed with water, and dried at 110°C . to produce a lustrous golden product.

Microscopic examination by reflected light revealed a smooth and uniform stannic sulfide
15 coating on the mica flakes.

EXAMPLE 18

SnS_2 -Coated Mica Pigment with Red Reflection Color

The procedure of Example 17 was followed, except that the quantity of mica flakes was reduced to 24 parts. After drying at 100°C . and incorporating in a nitrocellulose film, the SnS_2 -coated mica flakes were seen to produce a red color when
25 examined by specular reflection and a yellow color when seen at other angles.

EXAMPLE 19

Reflective Element from SnS_2 -Coated Glass Spheres

The procedure of Example 17 was followed, except that the quantity of water was trebled and the mica flakes replaced by 580 parts of glass spheres with an average diameter of 30 microns and an index of refraction of approximately 1.5.
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Incorporation in a clear paint vehicle produced a yellow coating material of very high reflectivity.

EXAMPLE 20

Pigment of CdS -Coated Mica

Cadmium chloride (33.3 parts) and thioacetamide (14 parts) were dissolved in 800 parts of water. To the solution were added 48 parts of mica flakes. The suspension was brought to pH 3.0 with hydrochloric acid.
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The reaction mixture was thereafter heated to boiling with agitation, and refluxed for 90 minutes, after which the cadmium sulfide-coated mica was filtered, washed with water, and dried at 110°C . to produce a lustrous golden pearl product.
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Microscopic examination by reflected light revealed a smooth and uniform cadmium sulfide coating on the mica flakes.

The foregoing examples describe specific procedures for the preparation of the sulfide-coated reflective elements hereof. Comparable coatings may be obtained under a wide variety of conditions. Hence, the compositions of the coating media, the temperature and duration of the heating of such media, and the time and duration of the preferred heat-treatment of the separated elements, may
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each be widely varied. The present invention may also be effected by use of a sequence or series of steps for building up a thick film comprising a plurality of zinc sulfide layers, rather than the procedure described for forming a single thickness layer.

WHAT WE CLAIM IS:—

1. A particulate reflective element comprising individual particles having maximum dimensions up to 10 millimeters and having high reflectivity and a nacreous lustre, wherein each particle includes a substrate which is constituted of mica, glass, plastic, or a lacquer- or resin-coated substance, said substrate having deposited thereon at least one layer of a water-insoluble metal sulfide, said layer having an optical thickness Nd from 40 to 1,000 millimicrons, wherein "N" is the index of refraction of said layer and "d" is the thickness thereof, and said particles having maximum dimensions up to 10 mm.

2. The element according to claim 1, wherein said water-insoluble metal sulfide is zinc sulfide.

3. A nacreous pigment constituted of particulate platelets having maximum dimensions of from 3 to 100 microns and substantially smooth surfaces, each of said platelets including a mica substrate and a pair of high refractive index layers formed on the opposite faces of said substrate constituted of a water-insoluble metal sulfide, said layers having substantially uniform optical thicknesses Nd of from 40 to 1,000 millimicrons, wherein "N" is the index of refraction of the layer and "d" is the thickness thereof.

4. A nacreous pigment according to claim 3, in which the mica substrates are mica platelets of a size passing through a screen of from 150 to 400 openings per lineal inch and of a surface area of from 2 to 6 square meters per gram as determined by the B.E.T. method.

5. A nacreous pigment according to claim 3 or 4, wherein each of said mica platelets is of a size passing through a screen of from 200 to 400 openings per lineal inch.

6. A nacreous pigment according to claim 3, 4 or 5, wherein the water-insoluble metal sulfide is zinc sulfide.

7. A nacreous pigment according to claim 6, for producing color by light interference phenomena, in which each of the high refractive index layers on each of said mica substrates has a substantially uniform thickness of from 200 to 650 millimicrons.

8. A nacreous pigment according to any one of claims 3 to 7, in which each of the high refractive index layers on each of said mica substrates is luminescent.

9. A process for preparing a particulate reflective element comprising individual particles having maximum dimensions up to 10 millimeters, which comprises:

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- (a) suspending smooth, plate-like supporting substrates for said particles in an aqueous solution containing (1) a water-soluble salt of a metal having a water-insoluble sulfide and (2) an organic sulfur-containing compound which releases sulfide ions in aqueous media, in an aqueous dispersion, said substrates being constituted of mica, glass, plastic or a lacquer- or resin-coated substance;
- (b) heating the resulting reaction mixture at temperatures of from 60°C. to the boiling point of the mixture for a period of from 1/4 to 5 hours, with agitation, to produce a sulfide coating on said substrate particles while maintaining the same in suspension;
- (c) separating the reflective particles thereby produced from said suspension;
- (d) drying said particles to produce a light stable, reflective material.
10. A process according to claim 9, wherein the dry particulate reflective materials are heated at temperatures of from 200° to 1,000°C. for periods of from 1 to 4 hours to increase their light stability.
11. A process according to claim 9 or 10, in which said organic sulfur-containing compound is constituted of thioacetamide, thiourea, thioglycollic acid, thioacetic acid, thioformamide or thiosalicylic acid, said water-soluble metal salt being a zinc salt which produces zinc sulfide in said aqueous dispersion.
12. The process according to claim 9, 10 or 11, wherein the water-soluble salt is a water-soluble zinc salt in an amount of from 0.25 to 7.5% of the solution.
13. The process according to claim 9, 10, 11 or 12, wherein the substrate is a mica substrate of a size passing through a screen of from 150 to 400 openings per lineal inch and of a surface area of from 2 to 6 square meters per gram as determined by the B.E.T. method.
14. The process according to any one of claims 9—13, wherein the reflective element has major dimensions of from 3 to 100 microns.
15. A nacreous pigment substantially as hereinbefore described.
16. A nacreous composition comprising a light-transmitting supporting medium having as a nacre-producing substance therein, the nacreous pigment according to any one of claims 3 to 8 or 15.
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